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The electrochemical oxidation of β-silyl-substituted arylsulfides and arylselenides

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Abstract—The oxidation of ring-substituted aryl(timethylsilylmethyl)sulfides and aryl(trimethylsilylmethyl)-selenides (R = H, Me, MeO, Cl, Br) in MeCN consists of a reversible electron transfer followed by the dimerization of the primary cation radicals and the rupture of the C_{sp^3}-chalcogenide bonds of the dicationic intermediate (E + C2 + C1 + E scheme). In MeOH, the oxidation leads to $PhSCH_2OMe$ and $PhSe-CH_2OMe$ resulting from the cleavage of the C—Si bond. The diaryldichalcogenides, which are the main products in MeCN, are practically absent. The electrochemical reactivity of arylchalcogenides is determined by their electronic structure. The specificity of the latter is a decrease in the role of the transmission of the electronic effects through the aromatic ring and an increase in the susceptibility of the heteroatom to direct electronic effects when going from ArSMe to ArSeMe and to their silylated derivatives.

Key words: electrooxidation, reactivity, cation radicals, silicon organic compound, arylselenides, arylsulfides.

INTRODUCTION

The decrease of the oxidation potentials of organoelement compounds and the change of the character of chemical reactions following their oxidation, that both result from the influence of the Me_3Si group, situated in the β position to the heteroatom (so-called the β-effect), is an important and widely investigated problem of organoelement chemistry. Since 1971, when the role of the β-effect in the oxidation of amines has been studied by Cooper and Owen [1], the large number of works appeared devoted to the establishment of the nature of this effect and of its role in the electrooxidation of various organic compounds [2–5]. A number of the large-scale elecrosynthetic processes on the base of β-Me_3Si substituted compounds [6–9] has been reported. It was shown that the decrease in the oxidation potentials of amines, ethers and sulfides is caused by a rising of the HOMO's energy in starting molecules due to the donor resonance interaction of lone-pair electrons of the heteroatom and a bonding σ (C—Si) orbital, on one side, and by the stabilization of the intermediate cation radicals (CRs), on the other side. Besides, a partial redistribution of the electron density at the reaction site of intermediates can occur affecting the following reactions of these species.

For the group VIA organoelement compounds, the β-effect was studied in details for ethers, while the oxidation of sulfides was generally considered from the synthetic points of view. Donor hyperconjugative interactions are appropriately decreasing downwards the group because of an increase in the energy difference of the overlapping orbitals and for sulfides they were shown to be four times smaller than for ethers [10]. In organic selenides, the heteroatom, due to its large size and its very weak n–π conjugation with the aromatic moiety, is quite sensitive even to fine interactions with neighbouring groups; in some cases, these interactions can remarkably affect the electrochemical reactivity of such compounds [11].

The purpose of this work was to reveal the role played by the β-effect in the electrochemical behaviour of organic sulfides and selenides in oxidation

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